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PROVISIONAL APPLICATION FILING ONLY

PROCESS FOR RECOVERING ORGANIC COMPOUNDS FROM AQUEOUS STREAMS CONTAINING SAME

Background of the Invention

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The present invention relates to a process for recovering hydrophilic organic compounds from aqueous streams containing same by liquid-liquid extraction.

Many valuable hydrophilic organic compounds such as carboxylic acids,
10 sulfonic acids, polyhydroxy compounds, amino acids and amides are produced or
utilized within manufacturing processes involving aqueous streams. Examples include
production of carboxylic acids via fermentation processes and utilization of sulfonic
acids as catalysts for esterification reactions. Various methods, such as, for example,
steam stripping, liquid-liquid extraction, liquid-solid adsorption, chromatography and
15 membrane-based methods, are known for recovery of these valuable hydrophilic
compounds from aqueous liquor containing same such as, for example, fermentation
broths and waste water streams.

For example, U.S. Patent No. 5,426,219 (W. Lenhardt et al) discloses a process
20 for recovering an organic acid such as lactic acid from an aqueous solution thereof. The
process involves extracting the aqueous solution containing an organic acid with a
mixture consisting of water, a mineral acid in quantity effective to maintain pH of the
mixture between 1.0 and 4.5, and an oxygenated solvent which has limited solubility
with water and the aqueous solution to produce a solvent extract and a first raffinate.
25 The oxygenated solvent has from 6-8 carbon atoms and at least one hydroxyl, ester,
ketone, ether, carbonyl or amid group. The solvent extract is then back extracted with
an aqueous liquid to produce an organic acid-rich aqueous extract and an organic acid-
depleted solvent raffinate.

30 U.S. Patent No. 3,556,739 (A. Baniel et al) discloses a process for extracting a
technical-grade phosphoric acid with certain organic solvents selected from the group
of ethers, ketones and glycol ethers having from 2 to 15 carbon atoms. These solvents
(a) practically do not extract phosphoric acid from an aqueous solution thereof having
concentration of phosphoric acid below 35% by weight, and (b) extract a substantial
35 portion of phosphoric acid from an aqueous solution thereof having a concentration of
phosphoric acid greater than 35% by weight.

U.S. Patent No. 4,322,550 (J. Kimble) discloses a process for recovery of mercaptoalkanoic acids from an aqueous solution thereof by a liquid-liquid extraction operation using at least one alkanoic acid ester and an alkylene glycol ether.

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U.S. Patent No. 5,628,906 (R. Shinnar et al) discloses a liquid-liquid extraction process wherein a solution of a solute in a native solvent, for example water, is mixed with a primary solvent, which is soluble with the native solvent, and subsequently adding a modifier, which is insoluble with either the native or the primary solvent. By adding the modifier, the solubility of the primary solvent with the native solvent is changed, thereby causing a near instantaneous phase separation. The solute is concentrated in the primary-solvent-rich phase. Examples of some primary solvents are acetaldehyde, acetic acid, acetonitrile, butanoic acid, ethanol, formic acid, methanol, propanoic acid, 1-propanol, 2-propanol, 2-propanone, propenoic acid, pyridine and triethylene glycol dimethyl ether. Examples of some modifiers are 3-methylbutyl ester of acetic acid, benzene, cyclohexane, 1,2-dichloro ethane, methyl isobutyl ketone, tetralin and toluene.

U.S. Patent No. 4,954,260 (Z. Ludmer et al) discloses a phase-transition type of forward extraction process, but one that uses a change in temperature to induce the phase transition, rather than a change in solvent composition. It describes a multi-stage counter-current process in which phase transition from a single-liquid phase to two liquid phases occurs in each step. The required phase transition is induced through the use of internal heating and cooling coils or other heat transfer means in each stage. The process requires changing temperature in each stage in order to cross a liquid-liquid phase boundary in each stage.

U.S. Patent No. 6,229,046 B1 (A. Eyal et al) and U.S. Patent No. 6,320,077 B1 (A. Eyal et al.) disclose processes for separating lactic acid from a fermentation broth containing free lactic acid and lactic acid salts. Oxygenated solvents that have a multiple number of functional groups (such as alcohol and ether) are mentioned as useful provided they give favorable partitioning of lactic acid. These solvents, however, are not used as extraction solvent themselves but rather in admixture with a tertiary amine (trialkylamine), which is the extraction solvent.

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Known liquid-liquid extraction processes used to recover hydrophilic organic compounds from aqueous feeds tend to be expensive, because of having a large number of steps, unfavorable partitioning (uneconomically low K values), poor selectivity for the desired solute, or poor efficiency for recovery of the solvents used. An improved method for recovery of valuable hydrophilic organic compounds from aqueous streams has now been discovered. This method uses certain glycol ethers having specific partition ratio, value K, in known liquid-liquid extraction equipment.

Summary of the Invention

In one aspect, the present invention concerns a method for separating a hydrophilic organic compound from aqueous liquor comprising the steps of:

- (a) intermixing a sufficient quantity of a glycol ether with the aqueous liquor at a first temperature to form a suspension comprising an aqueous raffinate phase and a glycol ether extract phase comprising said glycol ether, water in saturated quantity, and a portion of the hydrophilic organic compound, the glycol ether having the formula



wherein R' is an alkyl group of 1 to 8, preferably 1 to 4, carbon atoms; R'' is, independently in each occurrence, hydrogen, methyl or ethyl; R''' is hydrogen, an alkyl group having from 1 to 4 carbon atoms, a propionyl or an acetyl group; and n is an integer between 1 and 4; with the proviso that R''' is methyl when R' and R'' are each methyl group, and wherein the glycol ether has an inverse solubility in water and the partition ratio, value K, for the hydrophilic organic solute is greater than 0.1, preferably greater than 0.5, more preferably greater than 1.0, most preferably greater than 1.5.

- (b) separating the glycol ether extract phase formed in step (a) from the aqueous raffinate phase,
- (c) heating the glycol ether extract phase obtained in step (b) to a second temperature which is higher than the first temperature to form a suspension

comprising an aqueous extract phase containing a portion of the hydrophilic organic compound and a glycol ether raffinate phase, and

- 5 (d) separating the glycol ether raffinate phase formed in step (c) from the aqueous extract phase.

In another aspect, the present invention concerns the above described method wherein step (d) is replaced with the following two steps:

- 10 (e) intermixing sufficient quantity of water with the mixture formed in step (c) to form a mixture of a glycol ether raffinate phase further depleted in the hydrophilic organic compound and an aqueous extract phase containing the added water and additional hydrophilic organic compound;

- 15 (f) separating the aqueous extract phase formed in step (e) from the glycol ether raffinate phase.

In another aspect the present invention concerns the above described methods wherein the step (c) is conducted in the presence of a hydrophobic organic solvent
20 selected from the group consisting of an alcohol having from 4 to 14 carbon atoms, a ketone having from 4 to 14 carbon atoms, a chlorinated hydrocarbon having from 2 to 6 carbon atoms, an aromatic compound having from 6 to 12 carbon atoms, an ether having from 6 to 19 carbon atoms, and blends thereof.

25 In another aspect the present invention concerns a method for separating a hydrophilic organic compound from an aqueous liquor comprising the steps of:

- 30 (a) intermixing a sufficient quantity of a glycol ether with the aqueous liquor at a temperature not more than 30 centigrade degrees above the lower critical solution temperature (LCST), preferably not more than 20 centigrade degrees above the LCST, and most preferably not more than 15 degrees above the LCST, to form a suspension comprising an aqueous raffinate phase and a glycol ether extract phase comprising said glycol ether, water in saturated quantity, and a portion of the hydrophilic organic compound,
35 the glycol ether having the formula



wherein R' is an alkyl group of 1 to 8, preferably 1 to 4, carbon atoms; R'' is, independently in each occurrence, hydrogen, methyl or ethyl; R''' is hydrogen, an alkyl group having from 1 to 4 carbon atoms, a propionyl or an acetyl group; an n is an integer between 1 and 4; with the proviso that R''' is methyl when R' and R'' are each methyl, and wherein said hydrophilic organic compound is selected from the group consisting of citric acid, lactic acid, formic acid, acetic acid, succinic acid, ascorbic acid, 1,3-propanediol, 1,2-propanediol, glucose, glycerin, and *p*-toluene sulfonic acid; and

- (b) separating the glycol ether extract phase formed in step (a) from the aqueous raffinate phase.

Brief Description of the Drawing

Figure 1 is a flow diagram for a particular embodiment of the present invention.

Detailed Description of the Invention

The method of the present invention is useful for recovery of valuable hydrophilic organic compounds produced via fermentation or otherwise produced or utilized within a manufacturing process in which said hydrophilic organic compounds must be recovered from a dilute aqueous solution at some point in the fermentation or manufacturing process. The method of the present invention is particularly useful for recovery of hydrophilic organic compounds that are difficult or impossible to recover directly via distillation because of their low volatility with respect to water or because of their thermal instability at distillation temperatures. The hydrophilic organic compounds that can be suitably recovered by the method of the present invention are compounds selected from the group consisting of carboxylic acids, sulfonic acids, polyhydroxy compounds, amino acids, and amides. Preferably, the hydrophilic organic compounds are selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, lactic acid, citric acid, benzoic acid, ascorbic acid, adipic acid, succinic acid, methacrylic acid, lauric acid, stearic acid, glycolic acid, glycerin, glucose, caprolactam, 1,3-propanediol, 1,2-propanediol, 2,3- butanediol, xylitol, *p*-toluene sulfonic acid, methane sulfonic acid, and dodecylbenzene sulfonic acid. More

preferably, the hydrophilic organic compounds are selected from the group consisting of formic acid, acetic acid, lactic acid, citric acid, benzoic acid, ascorbic acid, succinic acid, adipic acid, p-toluene sulfonic acid, methane sulfonic acid, dodecylbenzene sulfonic acid, glycerin, caprolactam, 1,3-propanediol, 1,2-propanediol, 2,3- butanediol and xylitol.

The hydrophilic organic compounds that are recoverable by the method of the present invention must exhibit a partition ratio, value K , greater than 0.10, preferably greater than 0.5, more preferably greater than 1.0, most preferably greater than 1.5. The partition ratio, value K , is defined in terms of Bancroft coordinates; that is, in terms of mass ratios (K = mass of hydrophilic organic compound per mass of glycol ether in the organic phase divided by the mass of hydrophilic organic compound per mass of water in the aqueous phase). The use of Bancroft coordinates is described in Perry's Chemical Engineers' Handbook (Robbins, L. A. and Cusack, R. W., "Liquid-Liquid Extraction Operations and Equipment," Section 15 in Perry's Chemical Engineers' Handbook, 7th ed., R.H. Perry and D.W. Green, editors, McGraw-Hill, New York, 1997). Expressing the partition ratio in terms of mass ratios is desirable because doing so simplifies the material balance and mass-transfer calculations used to analyze process performance, as equilibrium and operating lines tend to be linear over a wide concentration range. The partition ratio for a hydrophilic organic compound varies for each individual glycol ether and can be easily determined by a person of an ordinary skill in the art without undue experimentation.

Suitable glycol ethers for extracting hydrophilic organic compounds in the method of the present invention are selected from the group consisting of dipropylene glycol ethyl ether, tripropylene glycol ethyl ether, propylene glycol isopropyl ether, dipropylene glycol isopropyl ether, tripropylene glycol isopropyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether, tripropylene glycol n-propyl ether, propylene glycol t-butyl ether, dipropylene glycol t-butyl ether, tripropylene glycol t-butyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol n-pentyl ether, propylene glycol n-hexyl ether, butylene glycol methyl ether, dibutylene glycol methyl ether, ethylene

glycol n-butyl ether, ethylene glycol n-pentyl ether, ethylene glycol n-hexyl ether, ethylene glycol n-heptyl ether, ethylene glycol 2-ethylhexyl ether, diethylene glycol n-hexyl ether, propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, propylene glycol isopropyl ether acetate, propylene glycol n-propyl ether acetate, 5 propylene glycol n-butyl ether acetate, dipropylene glycol methyl ether acetate, dipropylene glycol ethyl ether acetate, ethylene glycol n-butyl ether acetate, propylene glycol isobutyl ether, dipropylene glycol isobutyl ether, tripropylene glycol isobutyl ether, ethylene glycol t-butyl ether, ethylene glycol isobutyl ether, ethylene glycol ethyl ether acetate, ethylene glycol isobutyl ether acetate, diethylene glycol ethyl ether 10 acetate, dipropylene glycol dimethyl ether, and diethylene glycol n-butyl ether acetate and blends thereof. These glycol ethers are well known in the art and various methods for their preparation are described in the literature and practiced commercially.

These glycol ethers exhibit inverse solubility in water such that the solubility in 15 water at 100 °C is at least 1 weight percent less than the solubility in water at -5 °C. This inverse solubility behavior can be attributed to temperature-sensitive hydrogen bonding. It is known that many glycol ethers exhibit a lower critical solution temperature (LCST) below which they are completely miscible with water. At 20 temperatures below the LCST, the glycol ether is able to form hydrogen bonds with water and this attractive interaction leads to complete miscibility. At temperatures above the LCST, hydrogen bonding is disrupted by increasing thermal energy and hydrophobic interactions between the glycol ether and water begin to dominate. This results in partial miscibility and a decrease in the solubility of the glycol ether in water with increasing temperature (termed inverse solubility). Depending on the particular 25 glycol ether, the LCST can be as low as -10 °C or as high as 100 °C.

The method of the present invention involves the following key steps: (a) intermixing an aqueous stream containing a hydrophilic organic compound with a sufficient amount of a glycol ether at a first temperature to form a suspension 30 comprising an aqueous raffinate phase and a glycol ether extract phase comprising said glycol ether, water in saturated quantity, and a portion of the hydrophilic organic compound (forward extraction); (b) separating the glycol ether extract phase formed in step (a) from the aqueous raffinate phase; (c) heating the glycol ether extract phase obtained in step (b) to a second temperature which is higher than the first temperature

to form a suspension comprising an aqueous extract phase containing a portion of the hydrophilic organic compound and a glycol ether raffinate phase (back extraction), and (d) separating the glycol ether raffinate phase formed in step (c) from the aqueous extract phase containing the hydrophilic organic compound. Furthermore, additional steps may be used to enhance the recovery of hydrophilic organic compound. This involves the following key steps: (e) intermixing sufficient quantity of water with the mixture formed in step (c) to form a mixture of a glycol ether raffinate phase further depleted in the hydrophilic organic compound and an aqueous extract phase containing the added water and additional hydrophilic organic compound; and step (f) separating the aqueous extract phase formed in step (e) from the glycol ether raffinate phase.

In this description of the invention, the term raffinate phase refers to a liquid phase that becomes depleted in hydrophilic organic compound due to transfer of a portion of the hydrophilic organic compound contained in that phase into another liquid phase. The other liquid phase is termed the extract phase. In the forward extraction process (step (a)), the aqueous phase is the raffinate phase and the glycol ether phase is the extract phase. In the back extraction process (step (c)), the glycol ether phase is the raffinate phase and the aqueous phase is the extract phase.

Thus, according to the present invention, a hydrophilic organic compound is extracted from an aqueous stream containing same by a liquid-liquid extraction process involving a forward extraction into a glycol ether extract phase conducted at a first temperature where the K value is effective for transfer of the desired solute into the glycol ether extract phase. This is followed by back extraction of the hydrophilic organic compound from the glycol ether extract phase into water conducted at a second temperature where the K value is lower, favoring partition of the hydrophilic organic compound into water. In certain cases, however, the K value can be the same for both forward and back extraction. The extraction method conditions are determined by the magnitude of the K value for the forward extraction and its temperature sensitivity.

If desired, the glycol ether used in the method of the present invention can be recovered and recycled into the process. The recovery and recycling of the glycol ether must be achieved with little loss of the glycol ether in order to achieve good process economics. Both aqueous raffinate phase and aqueous extract phase containing hydrophilic organic compound become saturated with the glycol ether during the extraction process. Typically, the amount of glycol ether dissolved in these aqueous

phases is in the range of from 0.5 to 20 percent by weight. The saturation amount of the glycol ether varies with the particular glycol ether used, the temperature and the presence of other organic components in the solution. It may be desirable to reduce the concentration of the glycol ether left in the aqueous raffinate and aqueous extract
5 phases to levels below the saturation concentration in order to minimize waste treatment requirements, to meet hydrophilic organic compound specifications, and to reduce the need for using additional amounts of glycol ether as make-up solvent. The recovery of glycol ether can be done by any known solvent recovery methods, such as steam stripping, addition of a hydrophobic co-solvent with the glycol ether to reduce
10 the solubility of the glycol ether in the aqueous phase, and extraction of the glycol ether out of the aqueous phase into a hydrophobic organic solvent that is more readily recovered from the aqueous phase.

In cases where the glycol ether used has high relative volatility, the glycol ether
15 can conveniently be recovered for recycle back into the process using steam stripping as the recovery method.

In cases where the glycol ether is not sufficiently hydrophobic and volatile, the steam stripping solvent recovery method is not suitable. In such a case, the addition of
20 a steam-strippable hydrophobic solvent to the aqueous phase containing residual glycol ether provides an efficient method for recovering the glycol ether for recycle back to the method. The hydrophobic solvent extracts the residual glycol ether from the aqueous phase into a second hydrophobic solvent phase. The hydrophobic solvent must have a reasonably high K value for the glycol ether recovery and must be sufficiently
25 hydrophobic and volatile to allow its subsequent removal from water via steam stripping.

The hydrophobic organic solvents that are useful for recovery of glycol ethers in the method of the present invention are selected from the group consisting of an alcohol
30 having from 4 to 14 carbon atoms, a ketone having from 4 to 14 carbon atoms, a halogenated hydrocarbon having from 2 to 6 carbon atoms, an aromatic compound having from 6 to 12 carbon atoms, and an ether having from 6 to 19 carbon atoms. Non-limiting illustrative examples of the hydrophobic organic solvent useful in the method of the present invention are 1-octanol, 2-ethylhexanol, 2-pentanone, 2-
35 nonanone, diisobutylketone, methylisobutylketone, methylene chloride, toluene, dichlorobenzene, and di-n-butyl ether and blends thereof.

The intermixing of the glycol ether with the aqueous stream in step (a) of the method of the present invention is conveniently carried out at a temperature between about -5°C and 80°C . The temperature should not be more than 30°C , preferably no more than 20°C , above the lower critical solution temperature (LCST). The temperature used is dependent upon the particular glycol ether used. The temperature at which the heating of the liquid organic phase in step (c) of the method of the present invention is carried out is higher than the temperature used in step (a). In general, this temperature shall be between 10°C and 120°C and will also depend on the particular glycol ether used.

The method of the present invention is advantageously carried out at atmospheric pressure, although higher and lower pressures may be used in certain cases.

A person of an ordinary skill in the art may readily select the amount of glycol ether and organic hydrophobic solvent that may be used. The glycol ether must be used in sufficient amount to extract a desired portion of the organic hydrophilic compound from the aqueous feed stream. This can be readily determined by experimentation. The required amount of glycol ether may be reduced by using known multi-stage countercurrent liquid-liquid extraction methods.

In general, the hydrophobic organic solvent should be used in sufficient amount to extract a desired portion of the dissolved glycol ether from the aqueous feed solution. This also can be readily determined by experimentation, and the required amount of hydrophobic organic solvent may be reduced by using known multi-stage countercurrent liquid-liquid extraction methods.

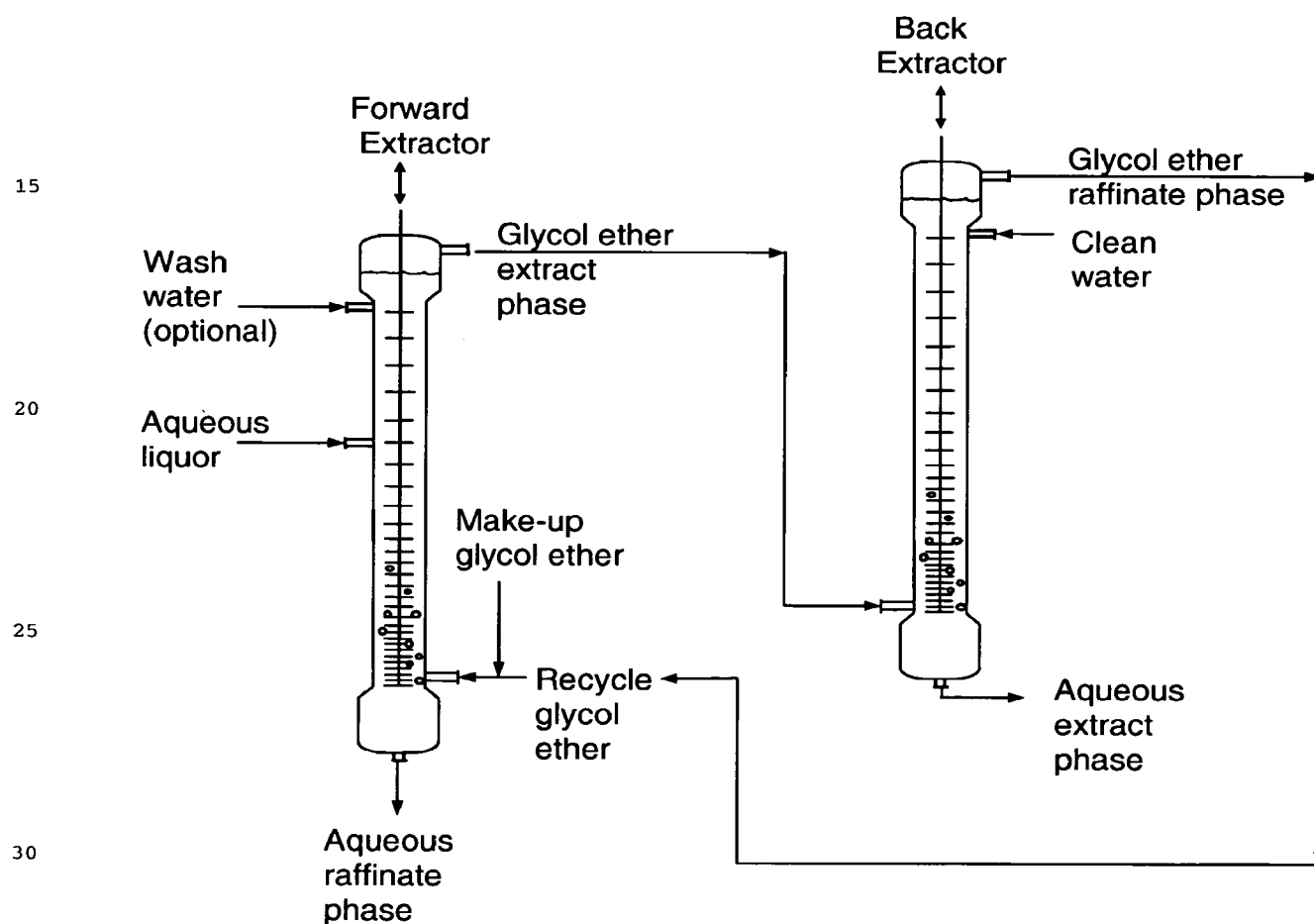
The method of the present invention can be carried out in a batch operation or continuously, and may be conducted in any conventional single stage or multiple stage liquid-liquid extraction equipment, including, for example, a countercurrent liquid-liquid extraction column.

The types of extraction equipment useful in the present invention are well known in the art and include, for example, a Karr column extractor and the like. The extraction process can additionally involve various types of known distillation and evaporation equipment for recovery of low-boiling or high-boiling glycol ethers, for

isolation of purified hydrophilic organic compound, or for recovery of a hydrophobic organic solvent, if used.

An embodiment of the present invention is illustrated in Figure 1 below wherein two Karr column extractors are used, one for the forward extraction step and the other for the back extraction step. This example is presented here to illustrate and clarify the invention and does not limit the application of the invention in any way.

Figure 1. Forward and Back Extraction



In the forward extraction step, as illustrated in Figure 1, an aqueous liquor containing the hydrophilic organic compound of interest is fed into the forward extraction Karr column extractor via an inlet located at the upper section of the column. The aqueous liquor forms an aqueous raffinate phase that moves down the column extractor and exits at the bottom. Glycol ether is fed into the forward extraction Karr column extractor via an inlet located at the lower section of the column, forming a glycol ether extract phase that moves up the column and exits at the top, countercurrent to the movement of aqueous raffinate phase. A small amount of wash water may be fed into the forward extraction Karr column extractor via an inlet located at the upper section of the column above the aqueous liquor inlet, to wash out any impurities such as sugars and the like, from the glycol ether extract phase exiting the column at the top. The wash water becomes part of the aqueous raffinate phase. As the aqueous raffinate phase moves through the forward extraction Karr column extractor, a portion of the hydrophilic organic compound transfers into the glycol ether extract phase. The aqueous raffinate phase exiting at the bottom of the column contains glycol ether in saturated quantity. The glycol ether extract phase exiting the column at the top contains water in saturated quantity and a portion of the hydrophilic organic compound that enters the Karr column extractor in the aqueous liquor. This forward extraction Karr column extractor is held at a low temperature at which the value K for the hydrophilic organic compound is high such that the amount of glycol ether needed to cause transfer of a desired portion of the hydrophilic organic compound out of the aqueous liquor into the glycol ether extract phase is reduced. The organic extract phase that exits the forward extraction Karr column extractor is fed into the second Karr column extractor for the back extraction. The same process may be conducted using other types of extraction equipment, including a mixer-settler cascade involving separate multiple liquid-liquid mixing stages and liquid-liquid separation stages. In general, the upper section of the forward extraction Karr column extractor shown in Figure 1 depicts the feed end of the forward extraction process, and the lower section of the forward extraction Karr column extractor shown in Figure 1 depicts the raffinate end of the forward extraction process. Figure 1 also illustrates the case in which the glycol ether extract phase has a specific gravity lower than that of the aqueous raffinate phase. This is normally the case, but in a few cases the specific gravity of the glycol ether extract phase may be greater than that of the aqueous raffinate phase. A person knowledgeable in the art of extraction will recognize how the invention illustrated in Figure 1 can be implemented using other types of extraction equipment and different relative specific gravities.

In the back extraction step, as illustrated in Figure 1, the glycol ether extract phase exiting the forward extraction Karr column extractor is fed into the back extraction Karr column extractor via an inlet located at the bottom section of the column. The glycol ether contained in this stream forms a glycol ether raffinate phase within the back extraction Karr column extractor that moves up the column and exits at the top. Clean water is fed into the back extraction Karr column extractor via an inlet located at the upper section of the column. The clean water forms an aqueous extract phase that moves down the column countercurrent to the movement of glycol ether raffinate phase and exits at the bottom. As the glycol ether raffinate phase moves through the column, a portion of the hydrophilic organic compound transfers into the aqueous extract phase. The glycol ether raffinate phase exiting the column at the top contains water in saturated quantity. The aqueous extract phase exiting the column at the bottom contains glycol ether in saturated quantity and a portion of the hydrophilic organic compound that enters the back extraction Karr column extractor in the glycol ether extract phase produced in the forward extraction Karr column extractor. The back extraction Karr column extractor is held at a higher temperature than the forward extraction Karr column extractor. At this higher temperature, the value K for the hydrophilic organic compound is generally lower than at forward-extraction conditions, and the amount of clean water needed to cause transfer of a desired portion of the hydrophilic organic compound into the aqueous extract phase is reduced. The partition ratio, value K , can be the same or different in the forward and back extraction steps; however, it is preferred that the value of K is lower in the back extraction step compared to the forward extraction step, since this allows a reduction in the amount of clean water and an increase in the concentration of hydrophilic organic compound in the aqueous extract phase. Glycol ether is recovered from the organic raffinate phase and is recycled back into the forward extraction Karr column. The same process may be conducted using other types of extraction equipment, including a mixer-settler cascade involving separate multiple liquid-liquid mixing stages and liquid-liquid separation stages. In general, the lower section of the back extraction Karr column extractor shown in Figure 1 depicts the feed end of the back extraction process; and the upper section of the back extraction Karr column extractor shown in Figure 1 depicts the raffinate end of the back extraction process. Figure 1 also illustrates the case in which the glycol ether raffinate phase has a specific gravity lower than that of the aqueous extract phase. This is normally the case, but in a few cases the specific gravity of the glycol ether raffinate phase may be greater than that of the aqueous extract phase.

A person knowledgeable in the art of extraction will recognize how the invention illustrated in Figure 1 can be implemented using other types of extraction equipment and different relative specific gravities.

5 If desired, additional equipment can be used in the method of the present invention such as additional extraction, distillation or evaporation equipment for purging impurities from the glycol ether raffinate phase prior to recycle back into the forward extraction step, for isolating hydrophilic organic compound from the aqueous extract phase, for recovery of dissolved glycol ether from the aqueous raffinate phase
10 and the aqueous extract phase, and for recovery and recycle of the hydrophobic solvent, when used. Such additional equipment and its use in liquid-liquid extraction methods are well known in the art. A person of an ordinary skill in the art would use such additional equipment or combination thereof in the method of the present invention in a manner known for use of such equipment in conventional liquid-liquid extraction
15 methods. The use of such additional equipment or combination thereof will depend on many factors, such as, for example, the nature of the hydrophilic organic compound, the nature of other compounds present in the aqueous feed, the nature of the glycol ether used, the use of the hydrophobic organic solvent, the costs associated with the use of glycol ether and/or hydrophobic solvent, the costs associated with the use of additional
20 equipment, and the overall economics of the entire process.

 In some cases the glycol ether extract phase comprising glycol ether and hydrophilic organic compound may be fed directly into distillation or evaporation equipment wherein the glycol ether is separated from the hydrophilic organic
25 compound, avoiding the back extraction step. This is not always practical; however, due to instability of the hydrophilic organic compound at the distillation conditions or because of high costs associated with the required equipment which may include expensive items such as high-vacuum equipment and wiped-film evaporators. When feasible, the glycol ether separated this way is recycled back into the forward extraction
30 step.

 The glycol ether dissolved in the aqueous raffinate phase exiting the forward extraction step, and glycol ether dissolved in the aqueous extract phase exiting the back extraction step, may be recovered using known methods, such as, for example by steam
35 stripping or distillation, or by extraction with a hydrophobic organic solvent and combined with the glycol ether recovered from the organic raffinate phase for recycle

back into the process. The efficacy of the various recovery methods depends upon the nature of the glycol ether dissolved in the aqueous phase, in particular the relative volatility of the glycol ether with respect to water and the partition ratio for extraction of glycol ether from the aqueous phase into a hydrophobic organic solvent phase. If a hydrophobic organic solvent is used, it should be one for which the saturation amount dissolved in the aqueous phase can be removed via steam stripping.

The purpose of using hydrophobic organic solvent in the invention can be two fold. In one case, the hydrophobic organic solvent can be used to extract dissolved glycol ether from the aqueous raffinate or aqueous extract phases as described above. In another case, it can be used in step (c) to lower the partition ratio, value K, for the hydrophilic compound. In a method of the present invention wherein a hydrophobic organic solvent is used in step (c), the organic raffinate phase comprising the glycol ether and the hydrophobic organic solvent exiting from the top of the back extraction step is fed into distillation equipment wherein the glycol ether is separated from the hydrophobic organic solvent. The separated glycol ether can be recycled back into the process.

All parts, percentages and ratios herein are by weight unless otherwise indicated.

The invention will be further clarified by a consideration of the following examples which are intended to be purely exemplary of the present invention.

Examples

Solubility experiments were conducted in a jacketed glass apparatus equipped with a thermowell, a motor-driven glass stirrer with short baffles, a water-cooled condenser, a top sampling port, and a bottom stopcock valve. The temperature in the apparatus was adjusted by circulating a 50/50 propylene glycol/water solution through the jacket with a Brinkmann Lauda RM6 Heating/Cooling Circulator attached to the apparatus with hoses. This set up allowed experiments to be run in the -15°C to 100°C temperature range, although most were conducted in the 0°C to 95°C range.

Example 1

Into the apparatus, through the sample port, were placed approximately 50.0g dipropylene glycol n-butyl ether (DPnB) and approximately 50.0g of a 10% aqueous lactic acid solution. The sample port was covered with a glass stopper. The water to the condenser was turned on, and the stirrer started and set to agitate the mixture at 800 rpm. The circulator was turned on and set for 0°C. The mixture was stirred continuously as it reached the set point and for ten minutes after the set point was reached. The stirrer was then turned off and the mixture was allowed to separate into two clear layers before collecting samples. Once the samples had been collected, the circulator was reset for 95°C where a new set of samples was taken.

At each temperature, four samples were taken (two from the top layer and two from the bottom layer). Samples of the bottom layer were collected through the bottom stopcock. Samples of the top layer were taken through the sample port in the lid using a disposable syringe with a long needle. Samples for the gas chromatography (GC) analyses were placed in tared 4-dram vials and weighed. Samples for titration were placed in 100-ml disposable titration cups and weighed. Approximately, 0.5g was collected for the GC analyses, and approximately 1.0g for the titration analyses.

Acid concentrations were determined by autotitration with 0.5 M KOH. Water and glycol ether concentrations were determined by GC with a Zebron ZB-1 column. The samples were diluted 5x with THF, the internal standard. The partition ratios, value K, for the forward extraction and the back extraction of lactic acid were calculated from the data generated from the samples and were found to be 1.2 and 0.47, respectively (see Table 1).

Example 2

Partition ratios were obtained for a 10% aqueous citric acid solution with ethylene glycol n-hexyl ether (Ehex) using the procedure described in Example 1. The partition ratios are shown in Table 1.

Example 3

Partition ratios were obtained for a 10% aqueous citric acid solution with propylene glycol n-propyl ether (PnP) using the procedure described in Example 1. The
5 partition ratios are shown in Table 1.

Example 4

Partition ratios were obtained for a 10% aqueous acetic acid solution with DPnB
10 using the procedure described in example 1. The partition ratios are shown in Table 1.

Example 5

Partition ratios were obtained for a 10% aqueous glycerin solution with DPnB
15 using the procedure described in Example 1. The partition ratios are shown in Table 1.

Example 6

Partition ratios were obtained for a 2% aqueous adipic acid solution with PnP
20 using the procedure described in Example 1. The partition ratios are shown in Table 1.

Example 7

Partition ratios were obtained for a 5% aqueous succinic acid solution with PnP
25 using the procedure described in Example 1. The partition ratios are shown in Table 1.

Example 8

Partition ratios were obtained for a 10% aqueous ascorbic acid solution with
30 PnP using the procedure described in Example 1. The partition ratios are shown in Table 1.

Example 9

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Partition ratios were obtained for a 10% aqueous 1,3-propanediol solution with PnP using the procedure described in Example 1. The partition ratios are shown in Table 1.

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Example 10

Partition ratios were obtained for a 10% aqueous glucose solution with PnP using the procedure described in Example 1. The partition ratios are shown in Table 1.

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Example 11

Partition ratios were obtained for a 10% aqueous citric acid solution (with 1% glucose present) with PnP using the procedure described in Example 1. The partition ratios are shown in Table 1.

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Table 1. Forward and Back Extraction Partition Ratios.

| Example | Glycol Ether | Hydrophilic Organic Compound | Forward extraction | | Back Extraction | |
|---------|--------------|------------------------------|--------------------|---------------------|------------------|--------------------|
| | | | Temperature (°C) | Partition Ratio (K) | Temperature (°C) | Partition Ratio(K) |
| 1 | DPnB | Lactic Acid* | 0 | 1.2 | 95 | 0.47 |
| 2 | Ehex | Citric Acid* | 5 | 0.82 | 80 | 0.23 |
| 3 | PnP | Citric Acid* | 45 | 1.3 | 95 | 0.44 |
| 4 | DPnB | Acetic Acid* | 0 | 1.79 | 80 | 0.76 |
| 5 | DPnB | Glycerin* | 0 | 1.1 | 80 | 1.1 |
| 6 | PnP | Adipic Acid** | 40 | 2.9 | 80 | 2.8 |
| 7 | PnP | Succinic Acid*** | 40 | 1.5 | 80 | 1.2 |
| 8 | PnP | Ascorbic Acid* | 50 | 0.5 | 80 | 0.3 |
| 9 | PnP | 1,3-Propanediol* | 55 | 1.0 | 80 | 0.7 |
| 10 | PnP | Glucose* | 20 | 0.14 | 80 | 0.04 |
| 11 | PnP | Citric Acid# | 45 | 1.0 | 80 | 0.5 |

* 10% aqueous solution

** 2% aqueous solution

5 *** 5% aqueous solution

10% aqueous solution in the presence of 1% glucose

10 Partition ratios for extraction of PnP from aqueous solution using various hydrophobic organic solvents were obtained in examples 12-24. These are examples for the recovery of a glycol ether from an aqueous phase using a hydrophobic organic solvent.

Example 12

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Into the apparatus, through the sample port, were placed approximately 40.0g 2-ethylhexanol and approximately 40.0g of a 10% aqueous PnP solution. The sample port was covered with a glass stopper. The water to the condenser was turned on, and the stirrer started and set to agitate the mixture at 800 rpm. The circulator was turned

on and set for 40°C. The mixture was stirred continuously as it reached the set point and for ten minutes after the set point was reached. The stirrer was then turned off and the mixture was allowed to separate into two clear layers before collecting samples. Once the samples had been collected, the circulator was reset for 60°C, 80°C, and 95°C where a new set of samples was taken at each temperature.

At each temperature, two samples were taken (one from the top layer and one from the bottom layer). Samples of the bottom layer were collected through the bottom stopcock. Samples of the top layer were taken through the sample port in the lid using a disposable syringe with a long needle. Samples were taken for gas chromatograph (GC) analyses and were placed in tared 4-dram vials and weighed. Approximately 0.5g was collected for the GC analyses.

Water, glycol ether, and hydrophobic organic solvent concentrations were determined by GC with a Zebron ZB-1 column. The samples were diluted 5 times with tetrahydrofuran (THF), the internal standard. The partition ratios, value K, at each temperature were calculated from the data generated from the samples and were found to be K=12.7 at 40°C, K=23.0 at 60°C, K=35.7 at 80°C, and K=42.7 at 95°C. The partition ratio at 95°C is shown in Table 2.

Example 13

Partition ratios were obtained for a 10% aqueous PnP solution with 1-octanol using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 14

Partition ratios were obtained for a 10% aqueous PnP solution with 2-pentanone using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 15

5 Partition ratios were obtained for a 10% aqueous PnP solution with methyl isobutyl ketone (MIBK) using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 16

10 Partition ratios were obtained for a 10% aqueous PnP solution with 2-nonanone using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 17

15 Partition ratios were obtained for a 10% aqueous PnP solution with di-isobutyl ketone (DIBK) using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 18

20 Partition ratios were obtained for a 10% aqueous PnP solution with methylene chloride using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 19

25 Partition ratios were obtained for a 10% aqueous PnP solution with tert-butyl methyl ether (MTBE) using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 20

35 Partition ratios were obtained for a 10% aqueous PnP solution with toluene using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 21

5 Partition ratios were obtained for a 10% aqueous PnP solution with dichlorobenzene using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 22

10 Partition ratios were obtained for a 10% aqueous PnP solution with n-butyl ether using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 23

15 Partition ratios were obtained for a 10% aqueous PnP solution with cyclohexane using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Example 24

20 Partition ratios were obtained for a 10% aqueous PnP solution with kerosene using the procedure described in Example 12. The maximum partition ratio obtained is shown in Table 2.

Table 2. Maximum Partition Ratio for Transfer of PnP from a 10% Aqueous PnP Solution into Various Hydrophobic Organic Solvents.

| Example | Hydrophilic Organic Solvent | Temperature (°C) | Partition Ratio (K) |
|---------|-----------------------------|------------------|---------------------|
| 12 | 2-Ethylhexanol | 95 | 42.7 |
| 13 | 1-Octanol | 95 | 22.9 |
| 14 | 2-Pentanone | 85 | 21.1 |
| 15 | MIBK | 95 | 17.3 |
| 16 | 2-Nonanone | 95 | 12.8 |
| 17 | DIBK | 95 | 12.2 |
| 18 | Methylene Chloride | 35 | 11.1 |
| 19 | MTBE | 45 | 10.2 |
| 20 | Toluene | 95 | 9.8 |
| 21 | Dichlorobenzene | 95 | 7.2 |
| 22 | n-Butyl Ether | 95 | 6.7 |
| 23 | Cyclohexane | 67 | 4.0 |
| 24 | Kerosene | 95 | 3.3 |

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Example 25

This is an example for the recovery of a glycol ether from water in the presence of the hydrophilic organic compound. Partition ratios were obtained for PnP and citric acid in the presence of same using 2-ethylhexanol and the procedure described in example 12. The aqueous charge consisted of 10% PnP and 10% citric acid. At 95°C, PnP had a partition ratio $K = 19.4$ and citric acid had a partition ratio $K = 0.03$. These results show that the glycol ether can be recovered effectively by the hydrophobic organic solvent without much loss of the hydrophilic organic compound.

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Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

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WHAT IS CLAIMED IS:

1. A method for separating a hydrophilic organic compound from an aqueous liquor comprising the steps of:

- 5 (a) intermixing a sufficient quantity of a glycol ether with the aqueous liquor at a first temperature to form a suspension comprising an aqueous raffinate phase and a glycol ether extract phase comprising said glycol ether, water in saturated quantity, and a portion of the hydrophilic organic compound,
- 10 the glycol ether having the formula



15 wherein R' is an alkyl group of 1 to 8 carbon atoms; R'' is, independently in each occurrence, hydrogen, methyl or ethyl; R''' is hydrogen, an alkyl group having from 1 to 4 carbon atoms, a propionyl or an acetyl group; and n is an integer between 1 and 4; with the proviso that R''' is methyl when R' and R'' are each methyl group, and wherein the glycol ether has an inverse solubility in water and the partition ratio, value K, for the

20 hydrophilic organic compound is greater than 0.1.

- (b) separating the glycol ether extract phase formed in step (a) from the aqueous raffinate phase,
- 25 (c) heating the glycol ether extract phase obtained in step (b) to a second temperature which is higher than the first temperature to form a suspension comprising an aqueous extract phase containing a portion of the hydrophilic organic compound and a glycol ether raffinate phase, and
- 30 (d) separating the glycol ether raffinate phase formed in step (c) from the aqueous extract phase.

2. The method of Claim 1, wherein the step (c) is conducted in the presence of a hydrophobic organic solvent selected from the group consisting of an alcohol having

35 from 4 to 14 carbon atoms, a ketone having from 4 to 14 carbon atoms, a chlorinated

hydrocarbon having from 2 to 6 carbon atoms, an aromatic compound having from 6 to 12 carbon atoms, and an ether having from 6 to 19 carbon atoms, and blends thereof.

3. The method of Claim 1, wherein the intermixing of the glycol ether with the aqueous liquor in step (a) is conducted at a temperature that is no more than 30 centigrade degrees above the lower critical solution temperature (LCST).
4. The method of Claim 1, Claim 2 or Claim 3, wherein step (d) is replaced with the following steps:
- (e) intermixing sufficient quantity of water with the mixture formed in step (c) to form a mixture of a glycol ether raffinate phase further depleted in the hydrophilic organic compound and an aqueous extract phase containing the added water and additional hydrophilic organic compound;
- (f) separating the aqueous extract phase formed in step (e) from the glycol ether raffinate phase.
5. The method of any one of Claims 1 to 4, wherein the steps of intermixing and separating phases are conducted in counter-current multistage extraction equipment.
6. The method of any one of Claims 1 to 3, wherein the aqueous raffinate phase separated in step (b) or the aqueous extract phase separated in step (d) are further contacted with a hydrophobic organic solvent or blends thereof to recover residual glycol ether.
7. The method of Claim 4 wherein the aqueous extract phase separated in step (f) is further contacted with a hydrophobic organic solvent or blends thereof to recover residual glycol ether.
8. The method according to any one of Claims 1 to 7, wherein the hydrophilic organic compound is a compound selected from the group consisting of carboxylic acids, sulfonic acids, polyhydroxy compounds, amino acids and amides.
9. The method according to Claim 8, wherein the hydrophilic organic compound is selected from the group consisting of formic acid, acetic acid, propionic acid, butyric

acid, lactic acid, citric acid, benzoic acid, ascorbic acid, adipic acid, succinic acid, methacrylic acid, lauric acid, stearic acid, glycolic acid, glycerin, glucose, caprolactam, 1,3-propane diol, 1,2-propanediol, 2,3- butane diol, xylitol, p-toluene sulfonic acid, methane sulfonic acid, and dodecylbenzene sulfonic acid.

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10. The method according to any one of Claims 1 to 7, wherein the partition ratio, K value, is greater in step (a) than in step (c).

11. The method of Claim 2, Claim 6 or Claim 7, wherein the hydrophobic organic solvent is selected from the group consisting of 1-octanol, 2-ethylhexanol, 2-pentanone, 2-nonanone, diisobutylketone, methylisobutylketone, methylene chloride, toluene, dichlorobenzene, and di-n-butyl ether and blends thereof.

12. The method according to any one of Claims 1 to 7, wherein the glycol ether is selected from the group consisting of dipropylene glycol ethyl ether, tripropylene glycol ethyl ether, propylene glycol isopropyl ether, dipropylene glycol isopropyl ether, tripropylene glycol isopropyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether, tripropylene glycol n-propyl ether, propylene glycol t-butyl ether, dipropylene glycol t-butyl ether, tripropylene glycol t-butyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol n-pentyl ether, propylene glycol n-hexyl ether, butylene glycol methyl ether, dibutylene glycol methyl ether, ethylene glycol n-butyl ether, ethylene glycol n-pentyl ether, ethylene glycol n-hexyl ether, ethylene glycol n-heptyl ether, ethylene glycol 2-ethylhexyl ether, diethylene glycol n-hexyl ether, propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, propylene glycol isopropyl ether acetate, propylene glycol n-propyl ether acetate, propylene glycol n-butyl ether acetate, dipropylene glycol methyl ether acetate, dipropylene glycol ethyl ether acetate, ethylene glycol n-butyl ether acetate, propylene glycol isobutyl ether, dipropylene glycol isobutyl ether, tripropylene glycol isobutyl ether, ethylene glycol t-butyl ether, ethylene glycol isobutyl ether, ethylene glycol ethyl ether acetate, ethylene glycol isobutyl ether acetate, diethylene glycol ethyl ether acetate, dipropylene glycol dimethyl ether, and diethylene glycol n-butyl ether acetate and blends thereof.

13. A method for separating a hydrophilic organic compound from an aqueous liquor comprising the steps of:

- (a) intermixing a sufficient quantity of a glycol ether with the aqueous liquor at a temperature not more than 30 centigrade degrees above the lower critical solution temperature (LCST) to form a suspension comprising an aqueous raffinate phase and a glycol ether extract phase comprising said glycol ether, water in saturated quantity, and a portion of the hydrophilic organic compound, the glycol ether having the formula



wherein R' is an alkyl group of 1 to 8 carbon atoms; R'' is, independently in each occurrence, hydrogen, methyl or ethyl; R''' is hydrogen, alkyl group having from 1 to 4 carbon atoms, a propionyl or an acetyl group; an n is an integer between 1 and 4; with the proviso that R''' is methyl when R' and R'' are each methyl, and wherein said hydrophilic organic compound is selected from the group consisting of citric acid, lactic acid, formic acid, acetic acid, succinic acid, ascorbic acid, 1,3-propanediol, 1,2-propanediol, glycerin, and *p*-toluene sulfonic acid; and

- (b) separating the glycol ether extract phase formed in step (a) from the aqueous raffinate phase.

14. The method according to Claim 13 wherein said temperature is not more than 20 centigrade degrees above the LCST.

15. The method of Claim 13 or Claim 14, wherein the steps of intermixing and separating phases are conducted in counter-current multistage extraction equipment.

ABSTRACT

A Method for a liquid-liquid extraction of hydrophilic organic compounds from aqueous solutions thereof is described. The method comprises the steps of:

- (a) intermixing a sufficient quantity of a glycol ether with the aqueous liquor at a first temperature to form a suspension comprising an aqueous raffinate phase and a glycol ether extract phase comprising said glycol ether, water in saturated quantity, and the hydrophilic organic compound, the glycol ether having the formula



wherein R' is an alkyl group of 1 to 8 carbon atoms; R'' is, independently in each occurrence, hydrogen, methyl or ethyl; R''' is hydrogen, an alkyl group having from 1 to 4 carbon atoms, a propionyl or an acetyl group; and n is an integer between 1 and 4; with the proviso that R''' is methyl when R' and R'' are each methyl group, and wherein the glycol ether has an inverse solubility in water and the partition ratio, value K, for the hydrophilic organic compound is greater than 0.1.

- (b) separating the glycol ether extract phase formed in step (a) from the aqueous raffinate phase,
- (c) heating the glycol ether extract phase obtained in step (b) to a second temperature which is higher than the first temperature to form a suspension comprising an aqueous extract phase containing a portion of the hydrophilic organic compound and a glycol ether raffinate phase, and
- (d) separating the glycol ether raffinate phase formed in step (c) from the aqueous extract phase.